COATINGS. ENAMELS

UDC 666.293

TINTED ONE-COAT GLASS ENAMELS FOR STEEL

E. A. Yatsenko,[1] E. B. Zemlyanaya,[1] and O. S. Krasnikova[1]

Translated from Steklo i Keramika, No. 1, pp. 28 – 30, January, 2006.

A basic formula for one-coat glass enamel is developed, which makes it possible to obtain a wide color range of coatings for steel products with good surface quality. A number of ionic colorants is tested, mainly compounds of *d*- and *f*-elements. The properties of coatings are studied: chemical resistance, adhesion strength, luster, and heat resistance. Their firing temperature is determined. The obtained glass enamels can be used in industrial production.

Single-layer enameling lately has been increasingly used in the production of household equipment, architectural and construction parts, pipes, and heat exchangers and is gradually displacing double-layer enameling that used to dominate. The new enameling method is promising in view of its saving of material and energy resources due to the decreased number of coat applications and firings. Single-coat enameling prevents warping of large-size details, furthermore; as the resultant thickness of the coating decreases, it becomes more elastic and impact-resistant [1]. Accordingly, one-coat enamels have to meet certain requirements, namely, have rather high chemical strength, heat resistance, and adhesion strength (since they simultaneous act as a ground layer and a surface coat) and at the same time have good decorative and aesthetic properties.

Some success has been achieved in this field; however, the technology for enameling steel using a low-melting single-coat enamel has not been developed yet. In this context, it is interesting to solve the new problem: develop compositions and technology for one-coat tinted glass enamel coatings with a decreased firing temperature for household steel products.

To developed a matrix formula for a single-coat enamel, we calculated frit compositions taking into account all requirements imposed on single-layer household enamels. The choice of components was based on the previous research of the South-Russian Technical University (NPI). Matrix frits were calculated for the following ratios of basic frit ÉSG-26 and low-melting single-layer white enamel: 1 : 99; 5 : 95, 10 : 90; 15 : 85, and 20 : 80, respectively. The enamel compositions considered are listed in Table 1.

All synthesized frits are clear, uniformly tinted glasses without visible crystallization, which indicates a high degree of glass formation. However, the most suitable CLTEs are found in frits 2 – 4 $(125 - 135) \times 10^{-7}\ K^{-1}$, as they are the closest to the CLTE of steel 08kp $(155 \times 10^{-7}\ K^{-1})$. A decreased melting temperature is seen in frits 2 and 3 (1180 – 1200°C), i.e., they can be regarded as low-melting.

[1] South-Russian State Technical University (NPI), Novocherkassk, Russia.

TABLE 1

Enamel composition	Weight content, %*											
	SiO_2	B_2O_3	Al_2O_3	TiO_2	Na_2O	K_2O	Li_2O	CaO	P_2O_5	Fe_2O_3	MnO_2	F^-
1	30.13	15.50	2.73	17.40	17.50	7.50	8.72	0.11	1.78	0.13	0.10	0.30
2	30.47	13.81	3.68	16.61	17.19	7.08	8.36	0.55	1.70	0.20	0.10	0.15
3	31.35	14.75	2.80	15.95	16.66	7.18	7.90	1.10	1.60	0.10	0.20	0.30
4	31.90	14.70	2.90	17.45	17.00	7.14	8.18	0.75	1.25	0.25	0.18	0.20
5	32.66	15.03	3.26	14.28	15.96	7.33	7.04	2.20	1.44	0.15	0.15	0.40

* Besides, all compositions contained 0.10% NiO.

0361-7610/06/0102-0029

TABLE 2

Group, subgroup	Colorant compound	Colorant ion	Type of colorant ion	Quantity of component introduced (above 100%), %
IB	Cu_2O	Cu^{1+}	*d*-element	1.5
IIB	$CdS + CdSO_3$	Cd^{2+}	The same	2.0
IIIB	CeO_2	Ce^{2+}	*f*-element	1.0
	CeO_2	Ce^{2+}	The same	2.0
	LaO_2	La^{4+}	″	1.0
	Pr_2O_3	Pr^{3+}	″	1.0
	Nd_2O_3	Nd^{3+}	″	1.0
	Y_2O_3	Y^{3+}	*d*-element	1.0
VB	V_2O_3	V^{3+}	The same	1.0
	Nb_2O_3	Nb^{3+}	″	1.0
VIB	Cr_2O_3	Cr^{3+}	″	1.0
VIIB	$MnSO_4{\cdot}5H_2O$	Mn^{2+}	″	1.7
	$MnSO_4 \cdot 5H_2O$	Mn^{2+}	″	3.4
	MnO_2	Mn^{4+}	″	1.0
	$MnCl_4 \cdot 4H_2O$	Mn^{2+}	″	2.3
VIII	NiO	Ni^{2+}	″	1.0
	Ni_2O_3	Ni^{3+}	″	1.0
	CoO	Co^{2+}	″	1.0
	$CoCO_3 \cdot H_2O$	Co^{2+}	″	1.8

The study of the chemical resistance, whiteness, and luster of synthesized enamels made it possible to identify the optimum formula for a single-coat enamel for steel. Thus, frit 2 became the basis for further studies, since it can provide a high-quality glass enamel coating, whose CLTE, chemical resistance, whiteness, and luster satisfy the requirements of GOST 24788–2001. The frit for the one-coat enamel has the following composition (wt.%): 30.00 – 31.20 SiO_2, 2.80 – 3.20 Al_2O_3, 14.00 – 15.00 B_2O_3, 0.50 – 0.60 CaO, 16.20 – 17.20 TiO_2, 1.50 – 1.90 P_2O_5, 17.00 – 17.40 Na_2O, 8.00 – 8.80 Li_2O, 6.00 – 8.00 K_2O, 0.03 – 0.07 MnO_2, 0.07 – 0.09 NiO, 0.06 – 0.08 Fe_2O_3, 0.10 – 0.20 CaF_2 (RF patent No. 2247084).

It is known that one of the main parameters of a high-quality one-layer coating is its high strength of adhesion to steel. In this case, apart from the enamel composition, pretreatment of metal is especially significant [2]. In order to analyze the effect of different methods for surface treatment of steel on the properties of one-coat enamels, we have studied the strength of adhesion of the steel-enamel composite using both traditional and new methods for preliminary treatment of steel before its enameling.

The lowest adhesion strength was observed in enameled samples subjected to the following methods of steel treatment before enameling: traditional (8%), chemical nickel-plating (20%), and boronizing (15%). Enameled steel samples treated by electrolytic zinc-plating, nickel-plating, copper-plating, and deep pickling had the strength of adhesion of the steel-enamel composition from 45 to 80%. The maximum adhesion strength values satisfying the state standard

TABLE 3

Duration of sample firing, min	Quality parameter K at firing temperature, °C				
	680	690	700	710	720
0.5	0	1	2	3.25	3.25
1.0	0.25	3	4	4.75	5.25
1.5	2	5	6	7	8
2.0	4.75	6.5	7	8.25	9.5
2.5	7	8	9	9.25	10
3.0	8.5	9.25	9.5	10	9.25
3.5	9	9.5	9.5	9	5
4.0	7.5	8	5.75	4	2.5
4.5	4.5	5	3	2	0
5.0	2	1	1	0.5	0

requirements were found in enameled steel samples treated by electrolytic nickel-plating and copper-plating (RF patent No. 2248410). To improve adhesion strength we tested the application of a copper film over a nickel film with the following ratio of respective films widths: 0.1 : 0.1, 0.3 : 0.2, and 0.2 : 0.3. This makes it possible to increase the strength of adhesion of nickel film to steel. The optimum ratio of metal film layers is 0.3 : 0.2 [2].

To obtain low-melting tinted enamels, *d*- and *f*-element colorants (Table 2) were introduced into enamel mixtures (above 100%).

All colorants introduced belong to the ionic colorant group, whose electron structure specifics consists in the fact that they have non-paired electrons or unfilled orbitals. When such cations are introduced, glass exhibits absorption spectra typical of the ionic condition of the particular component. The color shades imparted to glass depend on the band of the charge (electron) transfer from the 2*p*-orbital of oxygen to the *d*- or *f*-orbital of the colorant ion. It is established that such colorant compounds as Cu_2O, Pr_2O_3, Nd_2O_3, Cr_2O_3, $MnCl_4 \cdot 4H_2O$, and CoO impart the optimum shades and quality to the coating surface.

These one-coat tinted glass enamels are low-melting and their firing temperature is within 680 – 750°C.

The firing duration parameter has a significant effect on enameling efficiency. On the one hand, this parameter determines the level of electricity consumption and, on the other hand, the yield of acceptable products.

A mathematical model that has been developed earlier [3] describing the dependence of the strength of adhesion of enamel to steel on the chemical composition of enamel and the firing temperature makes it possible to determine a firing temperature that ensures the required adhesion strength (an important quality parameter) for each particular composition under a minimal electricity consumption.

However, the strength of adhesion is not the only quality parameters; it is just a necessary condition, but does not guarantee a satisfactory exterior appearance to the product, since an enameled surface, even one with the required strength of adhesion, may have defects (pores, burned-out color, sags, etc.). This happens when the firing duration is in-

TABLE 4

Sample*	Colorant compound	Quantity (above 100%), %	Firing temperature, °C	Luster, %	Adhesion strength, %	Heat resistance, number of thermal cycles of 400 – 20 – 400°C	Color
1	Cu_2O	1.5	680 – 730	61.7	75.0	6	Sky-blue
2	Pr_2O_3	1.0	680 – 740	65.0	76.0	6	Beige
3	Nd_2O_3	1.0	680 – 750	71.0	73.0	6	Cream
4	Cr_2O_3	1.0	680 – 750	76.0	54.8	7	Light green
5	$MnCl_4 \cdot 4H_2O$	2.3	690 – 740	74.0	48.3	6	Cream
6	CoO	1.0	690 – 740	78.0	58.0	6	Light brown

* Chemical resistance of all samples satisfies requirements of GOST 24788–2001.

sufficient (for instance, under low temperatures) or excessive (at higher temperatures). Consequently, it becomes necessary to develop a mathematical model that would take into account the effect of the temperature-time firing schedule on product quality.

The parameter usually accepted to estimate the quality of exterior appearance is the exterior appearance coefficient K graded according to a 10-grade scale. A surface is regarded as satisfactory when its exterior appearance coefficient has at least grade 8.

Earlier studies have demonstrated that the firing process is significantly nonlinear. Passive experiment data (Table 3) were used to calculate K. The dependence

$$K = f(\tau, t),$$

where τ is the firing duration and t is the firing temperature, was found as a set of several equations $K = f(\tau)$ for five temperatures in the considered interval (680 – 720°C).

The mathematical processing of experimental data using the Chebyshev polynomial method yielded the following regression equations:

Mathematical model	Temperature, °C
$K = 3.77083 - 12.276\tau + 11.1587\tau^2 - 2.8079\tau^3 + 0.210373\tau^4$	680
$K = -0.29167 + 2.17113\tau + 1.30973\tau^2 - 0.31041\tau^3 - 0.00583\tau^4$	690
$K = 1.14558 + 3.57876\tau^2 - 1.1213\tau^3 + 0.07839\tau^4$	700
$K = 3.51161 + 0.073371\tau^2 + 1.76935\tau^3 - 0.75421\tau^4 + 0.078445\tau^5$	710
$K = 3.54167 - 4.478\tau + 9.40122\tau^2 - 3.5295\tau^3 + 0.36014\tau^4$	720

It is found that the equations obtained adequately describe experimental data for a significance level equal to 5% and the degrees of freedom $f_1 = 5$ and $f_2 = 30$.

In order to determine the compliance of the optimal enamels to the requirements of GOST 24788–2001, we investigated their properties, such as chemical resistance, adhesion strength, luster, and heat resistance.

Chemical resistance was determined by spot testing with an acetic acid solution. Adhesion strength was measured on a LÉÉM instrument developed at the South Russian Technical University (NPI) [1]. All developed compositions had good strength of adhesion of the one-coat enamel to the substrate. The luster of coatings was assessed using a FB-2 photoelectric luster-meter designed at the South Russian Technical University (NPI). Heat resistance was determined by heating a fused sample over a burner for 5 min and subsequent abrupt chilling in cold water. The properties of resultant glass enamels are shown in Table 4.

Thus, synthesized coatings satisfy the requirements imposed on household steel ware and can be used in large-scale production. The obtained colors make it possible to expand the application area of one-coat glass enamel coatings and improve their decorative and consumer properties.

REFERENCES

1. *Technology of Enamels and Protective Coatings* [in Russian], Kharkov (2003).
2. E. A. Yatsenko, A. P. Zubekhin, and E. B. Klimenko, “Electrochemical methods for intensifying the strength of adhesion of one-coat glass enamels to substrate,” *Steklo Keram.*, No. 2, 25 – 28 (2004).
3. V. N. Kalinina and V. F. Pankin, *Mathematical Statistics* [in Russian], Vysshaya Shkola, Moscow (1998).